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FINAL REPORT - Part 1.

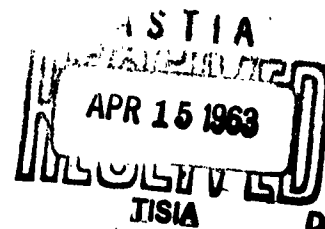
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OBJECTIVE OF THE WORK : Experiments on Electroluminescence.

AUTHORS : G.Bonfiglioli, P.Brovetto, A.Suardo.

TITLE : " Numerical analysis of Barrier - Injection Electro
luminescence".



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Summary.

In two previous Technical Notes, issued under the same Contract, there were exposed respectively the results of experiments about the EL of commercial (powder filled) cells, subjected to linear transients of voltage (see Tech. N. N.4) - and theoretical calculations of their behavior under the said excitation, assuming the basic viewpoint of Zalm about EL. (See Tech. N. N.7).

The equations obtained in this way, which are indeed fairly cumbersome, have been the subject of an accurate numerical analysis, reported in the present Tech.N. In this way the predictions of the theory developed in Tech.N. N.7, are compared to the results of Tech.N. N.4. A reasonable agreement is obtained at a qualitative level. This may indeed enhance our confidence in the assumptions of the theory, such as, for example, barrier injection and tunnel effect. On the other hand, powder filled cells do not look well suited to an accurately quantitative investigation, so that a definite judgement must be postponed to the moment when the results of similar experiments dealing with single crystals are available.

1.- INTRODUCTION.

The present Technical Note reports the results of a numerical analysis of the final equations of the previously issued Tech.N. N.7, entitled: "Calculations about Barrier-Injection Electroluminescence", so a comparison can be established with the experimental results exposed in the Tech. N. N.4, entitled: "Preliminary experiments on Electroluminescence of ZnS". The reader is therefore referred to the mentioned Technical Notes for every detail not reproduced in this text - in particular for the meaning of the symbols.

We remember only briefly the point of view - due to Zalm⁽¹⁾ - followed in the Tech.N. N.7. According to this point of view, EL is due to the establishment of a potential barrier at the interface conducting phase/ZnS, to tunneling through this barrier of electrons coming from the conducting phase, to their acceleration by the externally applied electric field which is strongly localized at the interface and, finally, to impact excitation of the activator centers by the accelerated electrons.

Successively, making use of some results obtained by Zalm on these grounds, we developed the calculation so as to evaluate the current density through an (admittedly cubic shaped) grain of the phosphor powder, when a linear transient of electrical potential is applied to the whole cell. Also the shape of the ensuing light pulse has been found. From Tech. N. N.7 we reproduce here the following e-

(1) P.Zalm, Philips Res. Rep. 11, 353 (1956).

equations we are going to make use of :

$$(1) \quad t = v_2 \frac{C_d + C_g}{C_d} \frac{1}{v} \left[1 + \frac{5}{3} \frac{\omega}{\lambda v C_d} v_2^{8/5} \exp(-\lambda v_2^{3/5}) \right]$$

correspon. to eq. (4.13);

$$(2) \quad i_c = \omega v_2 \exp(-\lambda v_2^{3/5}) , \text{ corresp. to eq. (4.5);}$$

$$(3) \quad \tau = v_m / \dot{v}, \text{ derived from fig. (4.a).}$$

2.- NUMERICAL ANALYSIS.

As stated, the meaning of the symbols is to be found in Tech.N. N.7. The values adopted for the various (geometrical and structural) parameters on which the values of the constants λ , ω , C_d , C_g depend are:

$E_F = 10 \text{ eV}$ (purely indicative of the order of magnitude)

$\epsilon = 10$
 $\epsilon_0 = 4$ } known from literature

$A = 1 \text{ eV}$ (as suggested by Zalm)

$\rho = \begin{cases} 10^{18} \text{ e/cm}^3 \\ 10^{19} \text{ e/cm}^3 \end{cases}$ The first value was actually suggested by Zalm, assuming to be approximately equal to the activator concentration

$d = 10^{-3} \text{ cm.}$

$d' = 0.5 \cdot 10^{-3} \text{ cm}$

$l = 1 \text{ cm}$ (to normalize the current intensity).

Several of these values, though reasonable, are largely arbitrary, and at least one of them, namely A , is likely to be wrong (actually, much too high); but there was no means of determining them more exactly at this stage of

the investigation. This is one of the reasons why commercial EL cells filled with powder phosphors are not well suited for quantitative studies - and by consequence the analysis reported here is not quite conclusive.

Using these values of the constants, eq.s (1) and (2) can be written as follows:

$$\text{CASE A (i.e. } \rho = 10^{18} \text{ e/cm}^3 \text{):}$$

$$(4) \quad t = 2.2498 v_2 \frac{1}{v} \left[1 + 1.9564 \cdot 10^{14} \frac{v_2^{8/5}}{v} e^{-17.10 v_2^{-3/5}} \right]$$

$$(5) \quad i_c / \eta_0 = 1.278 \cdot 10^{12} v_2 \exp(-17.10 v_2^{-3/5})$$

$$\text{CASE B (i.e. } \rho = 10^{19} \text{ e/cm}^3 \text{):}$$

$$(6) \quad t = 2.2498 v_2 \frac{1}{v} \left[1 + 4.914 \cdot 10^{14} \frac{v_2^{8/5}}{v} e^{-6.8076 v_2^{-3/5}} \right]$$

$$(7) \quad i_c / \eta_0 = 1.278 \cdot 10^{12} v_2 \exp(-6.8076 v_2^{-3/5}).$$

All the constant are expressed in CGS units.

The four function (4), (5), (6), (7) have been numerically evaluated by the Electronic Computer (I.B.M. 650) of the "Centro Calcolo Numerico" of the "Istituto Matematico" of Genova⁽²⁾.

The range of variation of the variables, the step chosen for them and the accuracy of the calculation were as follows:

Case A

$$\begin{aligned} 30 \leq \dot{V} \leq 3000 & \quad \text{step} = 120 \\ 0 \leq V_2 \leq 0.7 & \quad \text{step} = 0.0035 \end{aligned}$$

Case B

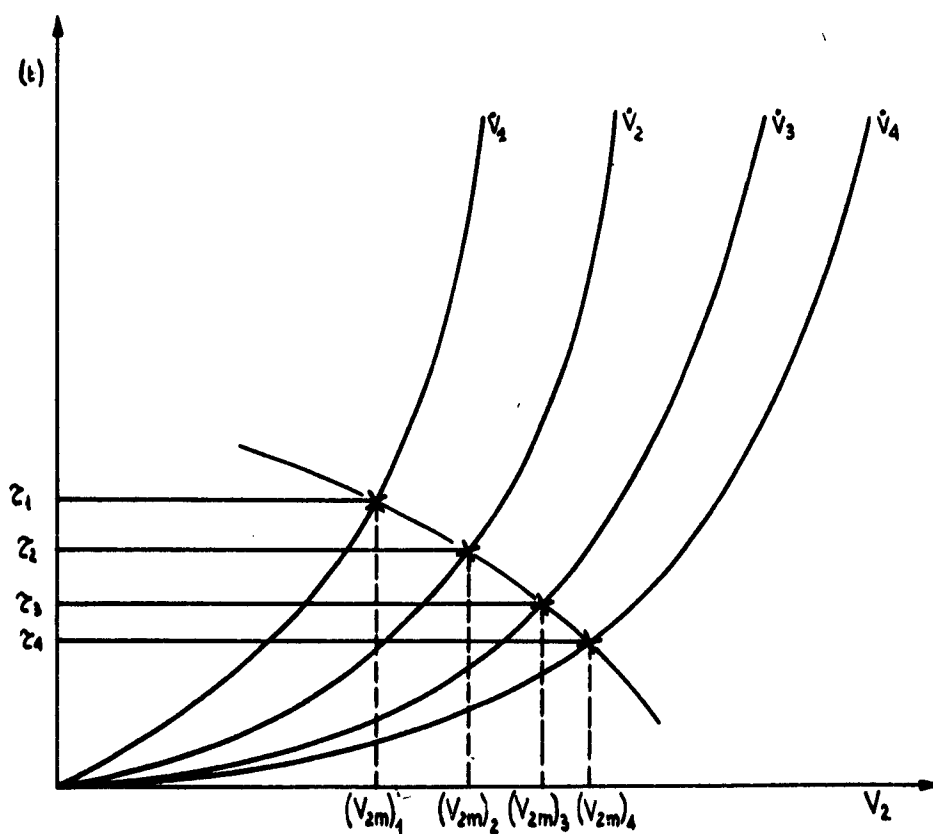
$$\begin{aligned} 6 \leq \dot{V} \leq 600 & \quad \text{step} = 24 \\ 1000 \leq \dot{V} \leq 3300 & \quad \text{step} = 333 \\ 0 \leq V_2 \leq 0.17 & \quad \text{step} = 0.00085 \end{aligned}$$

The results were given with at least 7 significant digits.

(2) It is a pleasure to gratefully acknowledge the help received from Prof.R.Malvano of the Istituto Fisico of the University of Genova and from Dr.G.Rebolia of the "Istituto Calcolo Numerico" in this phase of our work.

In both cases a plot has been made of t as a function of V_2 , using \dot{V} as a parameter.

From eq. (3) for a given value of \dot{V} and of the maximum voltage V_m applied to the cell, we evaluated the rising time τ of each linear transient. This time, τ , corresponds in the plot $t = t(V_2)$, to a value V_{2m} for the maximum voltage across a phosphor grain, that is: $V_{2m} = V_{2m}(\tau)$, as here schematically shown:



In this way a plot of V_{2m} as a function of \dot{V} has been obtained which represents the actual behaviour, schematically outlined in fig. 4.c of Tech. N. N.7.

Using this result and eq.s (5) and (7) yields finally i_{cm} , that is the maximum value of i_c , as a function of \dot{V} : $i_{cm} = i_{cm}(V_m, \dot{V})$. Plots of i_{cm} , or more precisely, of i_{cm}/η for case A and B are given in figg. (1) to (6). These plots have been made for various values of V_m , without paying attention to the actual magnitude of the voltage. In fact, our calculation makes use of an arbitrary value of the grain dimension and it does not specify the number of layers in series that constitute the cell. Therefore, in this calculation, the absolute values of the voltage found bear no definite relationship to the corresponding experimental values - and only the behaviour of i_{cm} vs. \dot{V} has actually to be considered as meaningful.

3.- DISCUSSION OF THE RESULTS.

Fig. (1) gives, for case A, and in semilogarithmic scale, i_{cm}/η vs. \dot{V} (up to 1000 V/msec), for 9 values of V_m (from 250 up to 900 Volt).

Fig. (2), for case B, gives again in semilogarithmic scale i_{cm}/η vs. \dot{V} for 8 values of V_m (from 60 up to 160 Volt).

Fig. (3), gives, for case A, a linear plot of i_{cm}/η vs. \dot{V} for 3 values of V_m (375, 400 and 420 Volts).

Fig. (4) does the same for case B and for 3 values

of V_m (75, 90, 100 Volt).

Fig. (5) gives for case A, an expanded scale linear plot of i_{cm}/η vs. V for $V_m = 300$ Volts.

Fig. (6) does the same for case B and for $V_m = 70$ Volts.

This way of presenting the results may perhaps look a bit involved but it is impossible to offer a clearer landscape of the behaviour of i_{cm}/η vs. V for different values of V_m and ρ . In fact, both these parameters have such a tremendous influence on the current value (as it could besides be inferred from the analytical expressions (1) and (2)) that a very tedious trial procedure has been necessary in order to identify the interesting range of variation of V_m and the reasonably possible values of ρ to be considered in the calculation.

At any rate these results, and in particular those of Figg.(3) and (4) that have been selected as the best ones, are to be directly compared with the experimental results shown in fig. (1) of Tech.N. N.4.

The two main points to compare are: the saturated behaviour as V grows bigger, and the ratio of the saturated values of i_{cm}/η for different values of V_m .

Both these points are qualitatively well met by the theoretical curves, but it is evident that no quantitatively satisfactory agreement is obtained.

As it can be seen, from the previous numerical results, the ratios of i_{cm}/q_n at various values of V_m differ from the experimental ones (see Tech.N. N.4) by a factor of the order of some units (3+4) for V large enough.

Let us now make some important remarks on this point.

Consider the dependence of i_c on V_2 :

$$i_c = i_c(V_2) \quad (8)$$

This is a tremendously increasing relationship (Cfr eq.2), especially if A is large enough as in the actual case ($A = 1eV$). Consider now the dependence of t on V_2 : $t = t(V_2)$ (Cfr eq.1). It has been shown that this relationship can be interpreted as:

$$V_m/\dot{V} = f(V_{2m}) \quad (9)$$

This functional dependence is also increasing at a tremendous rate, provided

$$i_c \propto \frac{5}{3} \frac{\omega}{\lambda V C_d} V_2^{8/5} \exp(-\lambda V_2^{-3/5}) \quad (10)$$

Using eq.(9) to express V_{2m} in terms of V_m (at a given \dot{V}) and putting the value so obtained into the eq. (8) yields finally:

$$i_c = \psi(V_m; \dot{V}) \quad (11)$$

which, does no longer show any very fast increasing behavior: the two tendencies mutually destroyed each other. If, on the contrary, eq.(10) were not verified, one would have obtained a tremendously steep rising of i_{cm} as a function of V_m (at given V).

We know that this behavior does not correspond to the experiment.

It follows from these premises that eq.(10) is actually verified and that the second part of the second member of eq.(1) namely the part containing the exponential, is the dominant one. It corresponds to the conduction current in the conductive branch of the equivalent circuit of the cell (Cfr Fig.4-b Tech.N. N.7).

We can therefore conclude with confidence that the conduction current prevails on the displacement one even in the saturated region (high V) of the curves of Fig.1 of Tech. N. N.4, where the displacement component is highest. This remark shows that it should be possible to account accurately for the experimentally observed ratios of i_{cm}/η at various V_m .

As a matter of fact the success was not so good, because the term $\frac{5}{3} \frac{\omega}{\lambda V C_d} V_2^{8/5} \exp(-\lambda V_2^{-3/5})$ was not large enough as compared to unity. The responsibility of this fact belongs to the small value of the exponential, due to the fact that, being λ too large, λ was by consequence very large itself (Cfr. eq.4.7 of Tech.N. N.7).

The assumption $A = 1$ eV, suggested by Zalm, is therefore definitely wrong and we must conclude that the true value of A must be substantially smaller.

Lowering the value of A , could allow to obtain a more reasonable (actually lower) value for χ even if ρ were lowered of some amount (remember that $\chi \propto A^{3/2} \cdot \rho^{-2/5}$; Cfr eq.4.7 of Tech.N. N.7).

This conclusion is favorable, since the value $\rho = 10^{19} \text{ e/cm}^{-3}$ looks definitely too large, corresponding to a very high concentration of the donors.

Finally let us comment on the fact that all this discussion has been developed assuming the view-point of Zalm, according to which the barrier at the interface is an equilibrium barrier. It is otherwise well known⁽³⁾ that complicated after effects and hysteresis phenomena affect the behavior of EL cells.

As a matter of fact, in our experiments of Tech. N. N.4 the reader can find a trace of such effects: namely the different behavior of the peaks of light when rising or falling transients are used. These differences cannot find any logical explanation in Zalm's views nor in our quantitative treatment based on his assumptions.

On the other hand, these are not very big differences.

Another topic, which should be taken into account,

(3) Cfr. G. Bonfiglioli, P. Brovotto, R. Malvano "On the relation between Frozen Polarization and EL of ZnS Cells". Summary Report Part B, Contract AF 61(052)-328, OAR, USAF.

is the relation between light and current, that is only approximately a linear relationship (Cfr Tech.N. N.7).

So the theory worked out in Tech.N. N.7 is only a first approximation - even though in our opinion work satisfactorily within these limits.

As already stated, if the quantitative aspect is to be pushed ahead, single crystals look the only suited subjects and we hope to be able to report shortly about experiments of this kind.

E R R A T U M

In the following figures, instead of $N = 10^{18}/\text{cm}^{-3}$, $N = 10^{19}/\text{cm}^{-3}$
please read respectively: $\rho = 10^{18} \text{ e}/\text{cm}^{-3}$, $\rho = 10^{19} \text{ e}/\text{cm}^{-3}$.

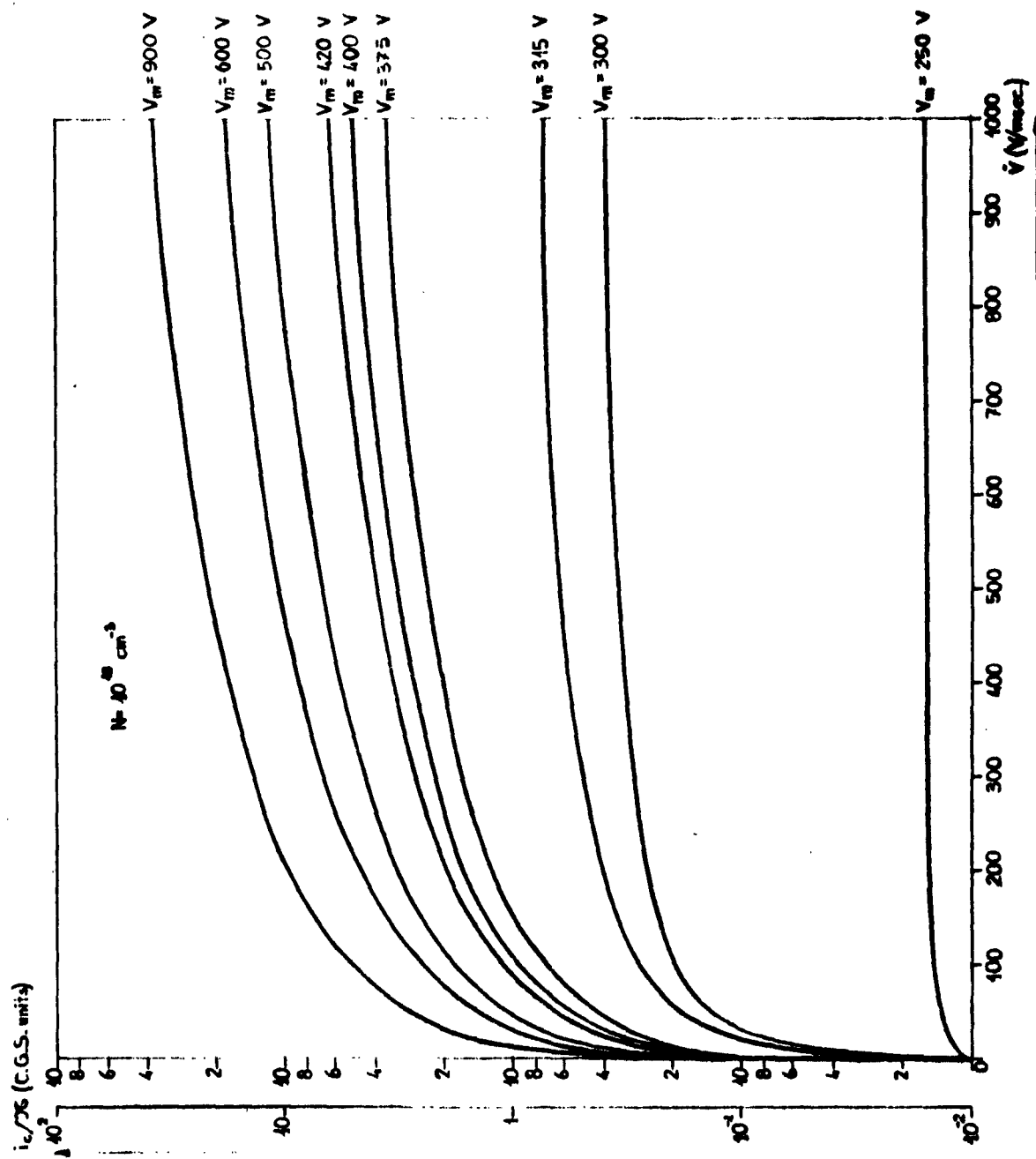


Fig. 4

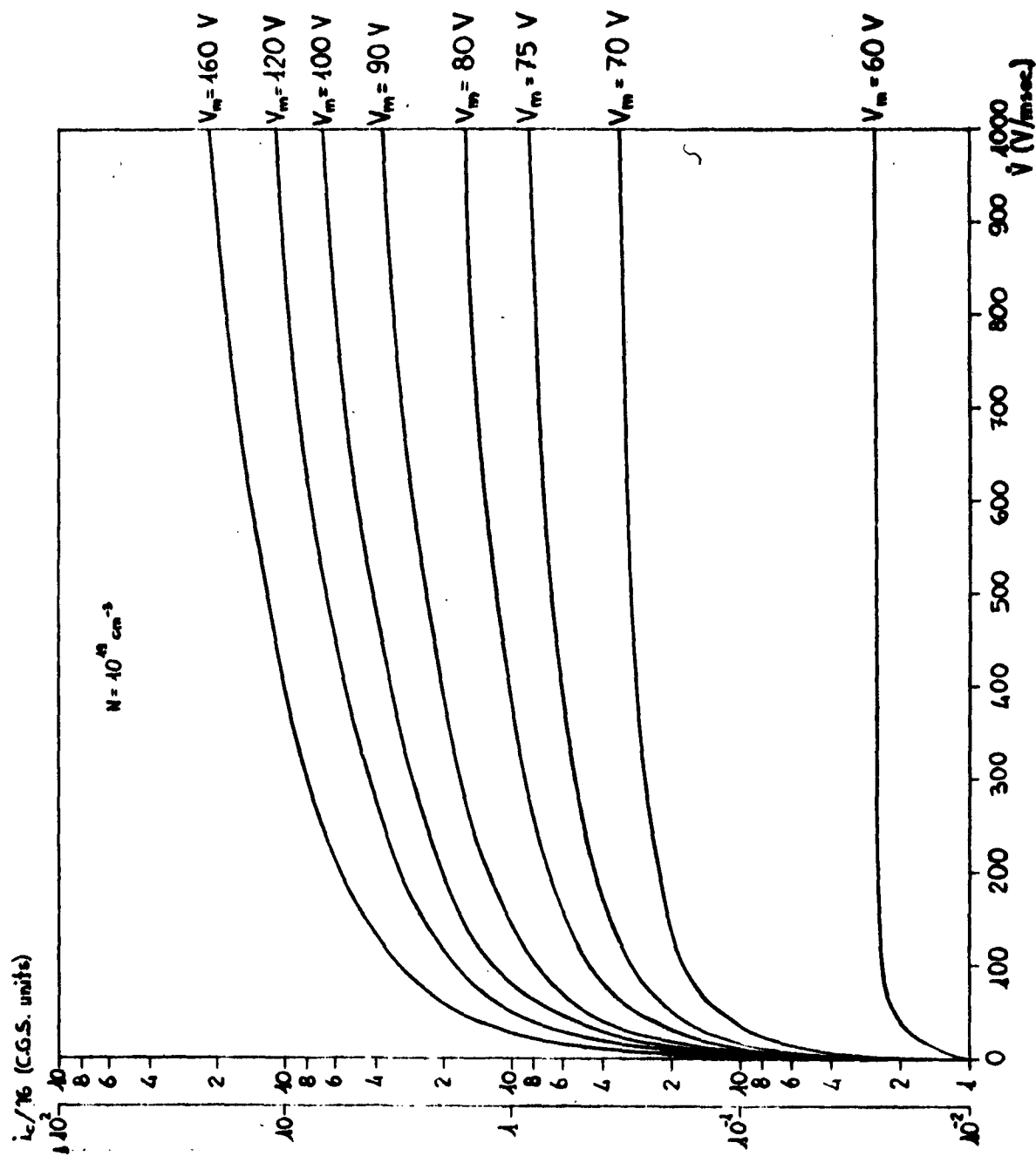


Fig. 2

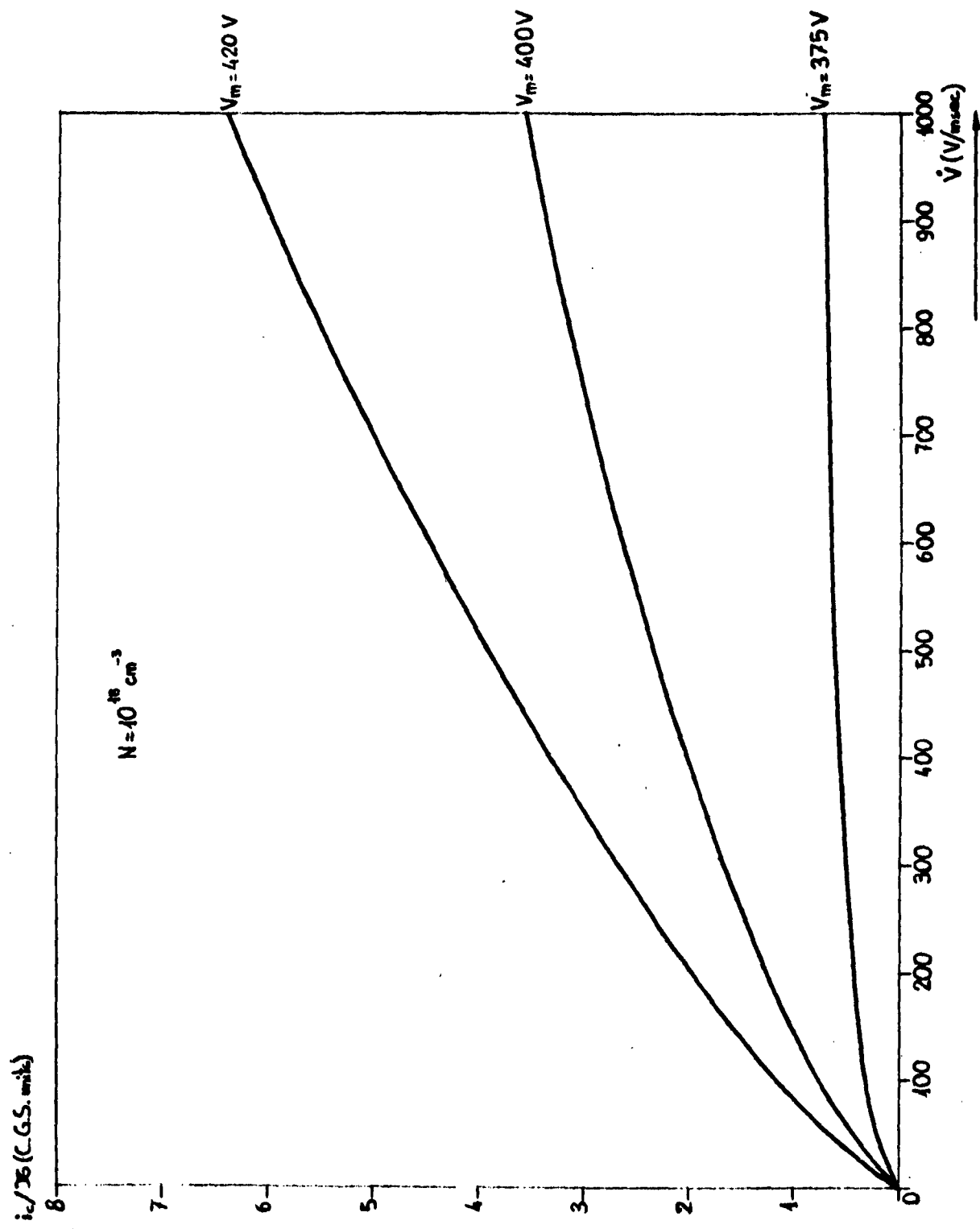


Fig. 3

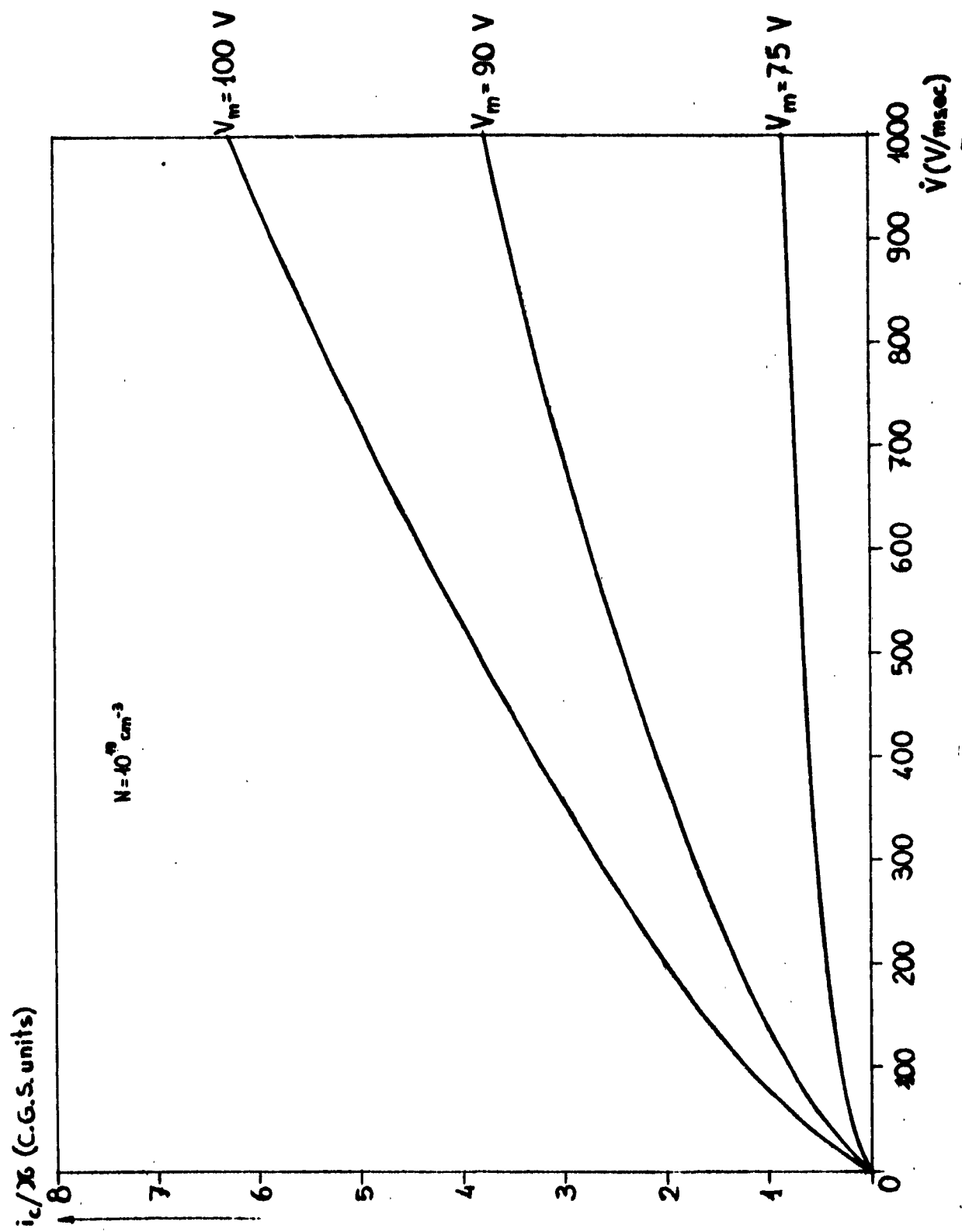


fig. 4

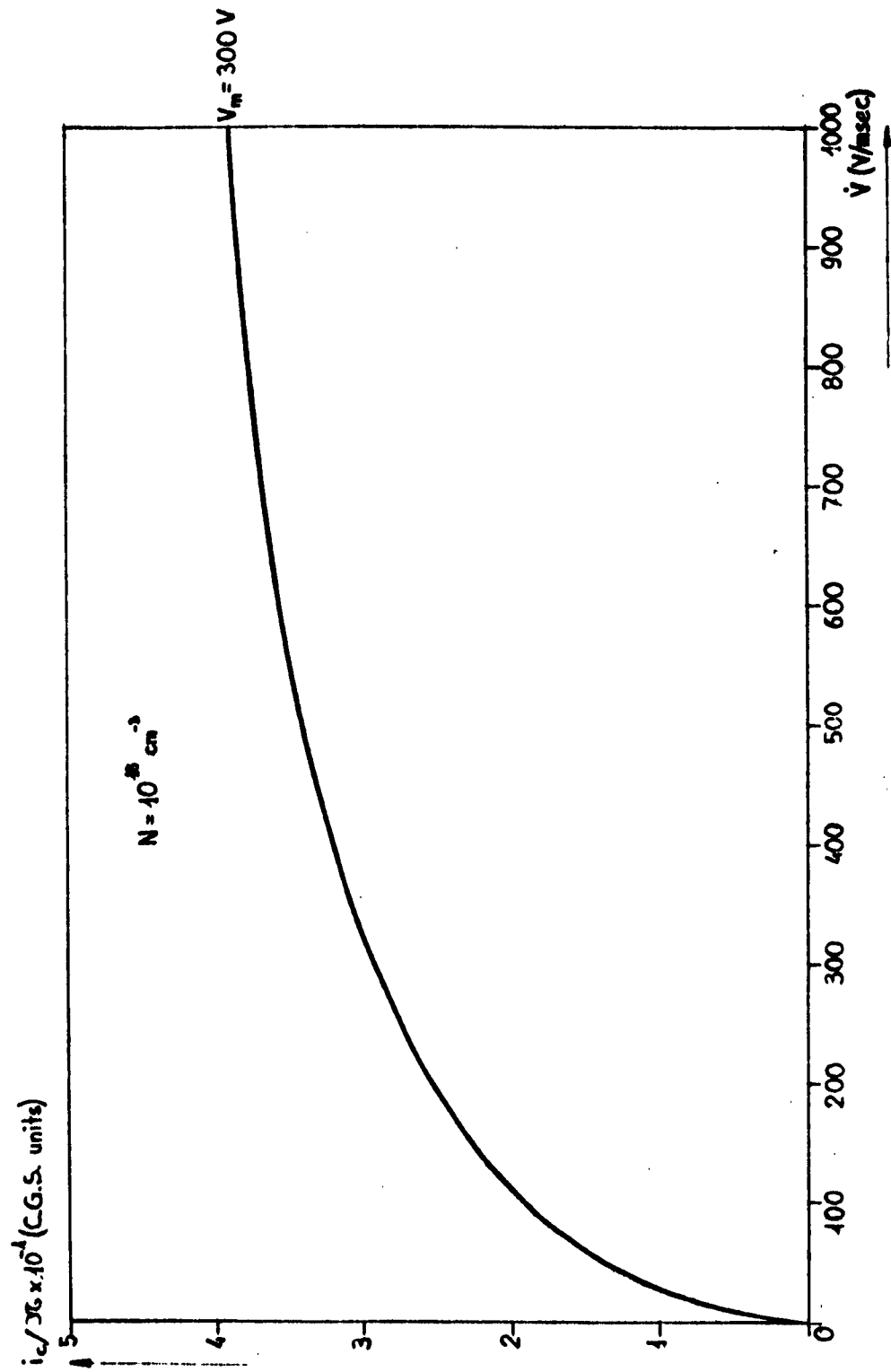


fig. 5

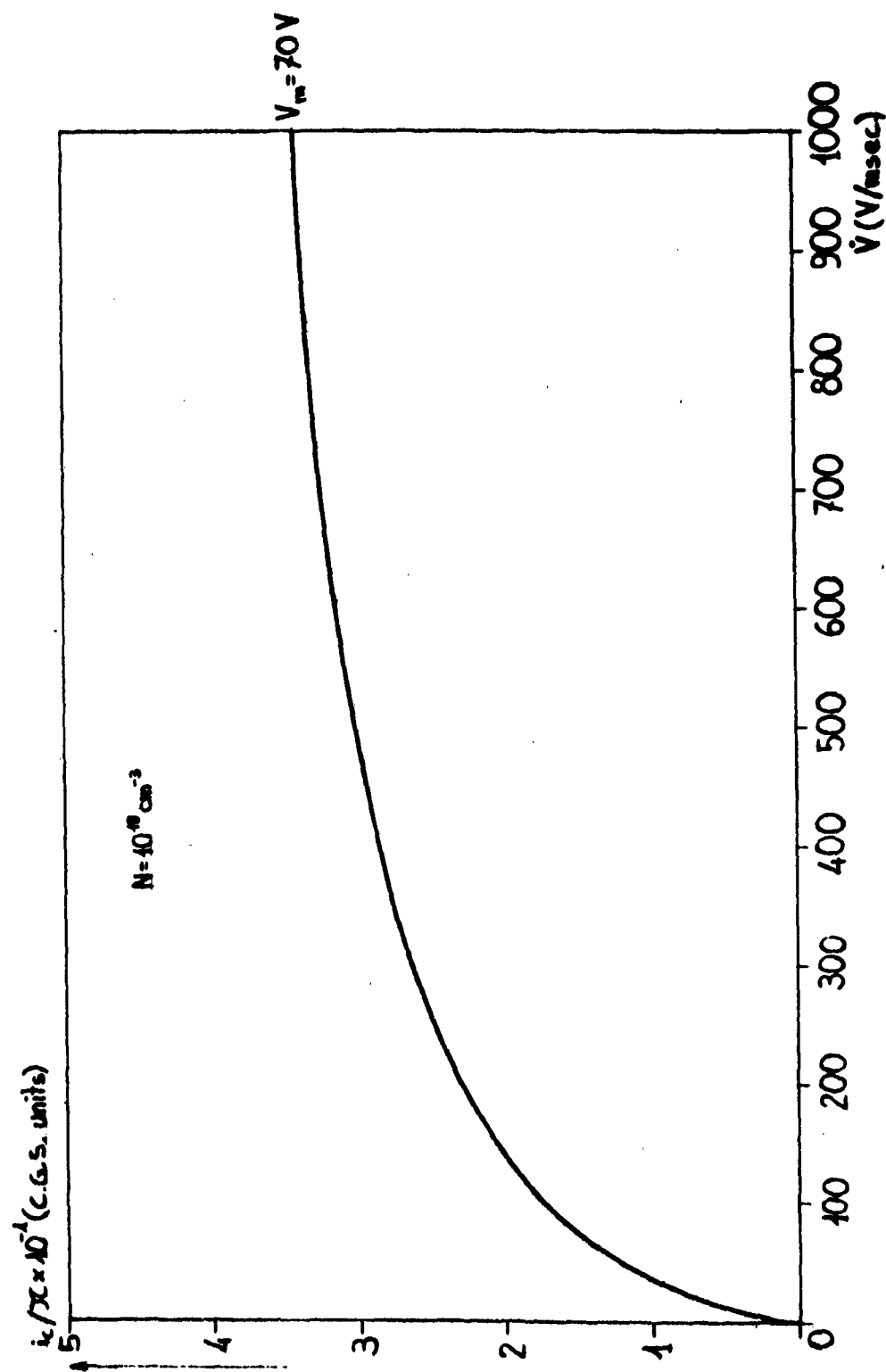


fig. 6